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(54) Abstract Title

Sol-gel method of manufacturing a silica glass article from silica with two particle sizes

(57) A sol-gel method of producing a silica glass article using a silica composed of two different sizes of particles comprising a) forming a sol of the silica b) aging (at 15-50°C) c) removing air bubbles and gelling and d) drying and heat treating the gel. The silica used is pyrogenic and has a particle size of from 5-100 nm (with a specific surface area of 50-400 m²g⁻¹) and is mixed with heat treated agglomerated particles of size 2-15 µm. The latter are formed by a) adding de-ionised water to the pyrogenic silica and mixing b) drying and selecting particles with a suitable diameter (10-850 µm) and c) heat treating at a temperature of 500-1200°C.

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**SILICA GLASS COMPOSITION
AND METHOD FOR MANUFACTURING SILICA GLASS USING THE SAME**

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The present invention relates to a silica glass composition and a method for preparing silica glass by a sol-gel process using the silica glass composition.

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Generally, silica glass is transparent, chemically inactive and has excellent characteristics such as thermal stability or strength and has a low thermal expansion coefficient. Such characteristics allow silica glass to be effectively useful for optical devices such as optical fiber or optical lens.

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An optical fiber is basically comprised of a core and a cladding having a refractive index different from that of the core so that total reflection of light occurs at the core. In connection with the total reflection of light, the refractive index of the cladding is about 1% lower than that of the core. A core having a refractive index of 1.47 and a cladding having a refractive index of 1.46 are generally used.

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To manufacture an optical fiber, an optical fiber preform comprised of a core rod and an overcladding tube surrounding the core rod is first fabricated. Then, the optical fiber preform is heat-treated and elongated to form the optical fiber.

A method for manufacturing an overcladding tube formed of silica glass using a sol-gel process will now be briefly described.

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First, silica particles are mixed with deionized water and a dispersant. Then, a binder and a plasticizer are added to the mixture and then mixed sufficiently to form a sol.

The sol is subjected to an aging-treatment for a predetermined time. Air bubbles are removed from the aging-treated sol, a gelling agent is added thereto and then poured into a mold.

When gelation is completed, the resultant gel is removed from the mold and then dried.

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Thereafter, the dried gel is heat-treated to remove organic substances in the gel. Subsequently, dehydroxylation and sintering processes are performed on the resulting gel, thereby completing an overcladding tube formed of silica glass.

Fumed silica is used as the silica particles. The fumed silica is pyrogenetic silica produced by pyrolyzing a silicon compound, e.g., SiCl_4 , and has a specific surface area of $50\sim 400\text{m}^2/\text{g}$ and average particle diameter of $5\times 10^{-2}\mu\text{m}$.

However, in the case of manufacturing silica glass using the fumed silica as the silica particle, the following problem may be generated.

Since the fumed silica is a microparticle having a small pore, it is difficult to disperse a large amount of fumed silica into the sol. Also, much time is required for removing air bubbles from sol and the viscosity of the sol increases excessively. Due to such characteristics of fumed silica, it is difficult to increase the content of silica solid in the sol to 50% or higher. Thus, the green density of the resultant obtained by removing the organic substance in the gel is limited to about 35% based on the density of the sintered body, which increases the shrinking ratio of the overcladding tube before and after the sintering process. Thus, it is practically difficult to manufacture a large silica glass tube. Also, a crack may be generated on the overcladding tube after being dried.

According to a first aspect of the invention, there is provided a silica glass composition comprising:

pyrogenetic silica having an average particle diameter of 5×10^{-3} to $1\times 10^{-1}\mu\text{m}$ and a specific surface area of 50 to $400\text{m}^2/\text{g}$; and

heat-treated silica as an agglomerate of the pyrogenetic silica, having an average diameter of 2 to $15\mu\text{m}$ and a specific surface area less than that of the pyrogenetic silica.

It is therefore an advantage of the present invention to provide a composition for preparing high-density silica glass having a reduced shrinking ratio without cracks.

According to a second aspect of the invention, there is provided a method for preparing silica glass comprising the steps of:

(a) forming a sol by mixing a dispersion medium and a mixture of pyrogenetic silica having an average particle diameter of 5×10^{-3} to $1\times 10^{-1}\mu\text{m}$ and a specific surface area of 50 to $400\text{m}^2/\text{g}$ and heat-treated silica as an agglomerate of the pyrogenetic silica having an average diameter of 2 to $15\mu\text{m}$, and a specific surface area less than that of the pyrogenetic silica;

- (b) aging the sol;
- (c) removing air bubbles from the aging-treated sol and gelling the same to form a gel; and
- (d) drying the gel and then heat-treating the dried gel.

5 It is an advantage of this aspect of the present invention to provide a method for preparing silica glass using the composition.

In the step (b), aging of the sol is preferably achieved at temperature in the range of 15 to 50 °C. If the temperature is above 50°C., silica glass is easily broken and if the temperature is below 15°C, aging reaction of the sol is too slow.

10 In step (a), the heat-treated silica is manufactured by the steps of:

(a-1) adding deionized water to the pyrogenetic silica and then mixing the resultant;

(b-1) drying the resultant obtained in step (a-1) and selecting particles having a predetermined particle diameter; and

15 (c-1) heat-treating the resultant obtained in step (b-1) at a temperature in the range of 500 to 1200 °C.

In step (a-1), the mixing ratio by weight of the pyrogenetic silica to the deionized water is 1:10 to 1:5, and more preferably 1:2 to 1:3. Here, if the content of the deionized water to the pyrogenetic silica is greater than the above-described
20 range, much time is required for the resultant obtained in step (a-1). Also, if the content of the deionized water to the pyrogenetic silica is less than the above-described range, dispersibility of the pyrogenetic silica is bad.

In step (b-1), the average particle diameter of the particle is in the range of 10 to 850 μm .

25 In the present invention, a mixture of general pyrogenic silica and heat-treated silica is used as a silica for silica glass. Here, the mixing ratio by weight of the pyrogenic silica and heat-treated silica is preferably 1:10 to 1:1. Here, if the content of the deionized water to the pyrogenetic silica is greater than the above-described range, cracking after drying occurs in the silica glass

30 . Also, if the content of the deionized water to the pyrogenetic silica is less than the above-described range, shrinking ratio is too high.

The heat-treated silica is an agglomerate of the pyrogenetic silica and has a larger particle diameter, i.e., 2~15 μm , a larger porosity and a smaller specific

surface area, than the pyrogenetic silica. Due to such characteristics of pyrogenetic silica, it is easy to disperse the pyrogenetic silica into the sol which increases the content of silica solid. And, the viscosity of the sol can be controlled appropriately. Also, air bubbles are easy to remove from the sol, so that cracks scarcely occur after the drying process and a shrinking ratio after the sintering process is reduced.

The silica glass composition according to the present invention includes a mixture of pyrogenetic silica and heat-treated silica. The composition also includes a dispersant, a plasticizer, a binder, a gelling agent and solvents, like the conventional silica glass composition.

The dispersant, the plasticizer, the binder, the gelling agent and the solvents are not specifically restricted but materials generally used in manufacturing the silica glass may be used. Also, the content levels of the respective materials are conventional ones.

As the dispersant, a quaternary ammonium hydroxide compound such as tetramethylammonium hydroxide or tetraethylammonium is used. These materials are helpful for silica to be homogeneously dispersed into the composition, and stabilize the silica-dispersed sol electrostatically.

As the plasticizer, polyhydric alcohol, for example, glycerin, ethylene glycol, or 2-methylpropane-1,2,3-triol is used.

As the binder, polyethyloxazoline, polymethyl oxazoline or polyacrylamide is used.

The gelling agent is an aqueous aliphatic ester of an acid selected from the group consisting of formic acid, lactic acid and glycolic acid.

A method for preparing heat-treated silica according to the present invention and a method for manufacturing an overcladding tube using the heat-treated silica prepared by this method will now be described in detail.

First, pyrogenetic silica is homogeneously mixed with deionized water and then dried to obtain silica dry powder monolith. The monolith is sieved to select only particles having a predetermined particle diameter. Here, the particle diameter is preferably 10 to 850 μm .

Thereafter, the resultant is heat-treated at a predetermined temperature to prepare noncrystalline silica powder having a diameter of 2 to 15 μm .

The temperature for heat treatment is preferably 500 to 1200 $^{\circ}\text{C}$, and more

preferably 600 to 900 °C. Here, if the heat-treatment temperature is below 500°C, the agglomerate of the pyrogenetic silica cannot be formed. If the heat-treatment temperature is above 1200°C, crystalline silica is produced, which is undesirable.

5 The mixture of the heat-treated silica prepared by this method and the pyrogenetic silica is mixed with a dispersion medium to form a sol. As the dispersion medium, deionized water is used, and a dispersant may be added if necessary.

Subsequently, a binder and a plasticizer are put into the mixture and then dispersed sufficiently for a predetermined time to prepare a sol. Then, the sol is left alone for a predetermined time for aging-treating.

10 Air bubbles are removed from the aging-treated sol, and a gelling agent is added thereto and then the resultant is poured into a mold. When gelation is completed, the resultant gel is removed from the mold and dried under constant temperature and humidity conditions.

Then, the dried gel is heat-treated to remove organic substances therefrom.

15 A hydroxy group is removed from the heat-treated gel under a chlorine (Cl₂) and oxygen (O₂) gas atmosphere, and then glassified at a sintering furnace being under a helium (He) gas atmosphere.

There now follows a description of preferred embodiments of the invention, with reference being made to the following non-limiting examples:

20 EXAMPLE 1

A mixture of 5600 g of fumed silica having specific surface area of about 50 m²/g and an average diameter of 4×10^{-2} μm and 14000 g of deionized water was homogeneously mixed in a ball-mill for about 24 hours to form a sol.

25 The sol was dried in an oven controlled at a temperature of 120 °C for about 24 hours. Then, the resultant was passed through a sieve (#20 mesh) to select silica particles having a diameter of 850 μm or less.

The silica particles were heat-treated in a furnace controlled at a temperature of 800 °C for 3 hours. It was observed that the obtained heat-treated silica had an average diameter of 3 μm and specific surface area of 45 m²/g.

30 EXAMPLE 2

A mixture of 5,600 g of heat-treated silica prepared in Example 1, 1,400 g of fumed silica, 5,700 g of deionized water and 700 g of tetramethylammonium

hydroxide aqueous solution (25 wt% in water) was homogeneously mixed for about 5 minutes.

Then, 21 g of polyethyloxazoline and 63 g of glycerin were put into the mixture and homogeneously mixed in a homogenizer at a rate of 8,000 rpm for about 2 minutes.

Subsequently, the mixture and 20 kg of glass ball were added to a ball-mill and mixed for about 6 hours. Next, the resultant was aging-treated in a cooling chamber controlled at a temperature of 10 °C for about 10 hours.

Air bubbles were removed from the aging-treated sol for about 20 minutes, and then 126 g of methyl formate was mixed thereto and poured the resultant into a mold.

After about 30 minutes, the resultant gel was removed from the mold. The obtained gel was dried in an incubator, that is, controlled at a temperature of 30 °C and a relative humidity of 85 %, for about 60 hours.

The dried gel was heated to 600°C at a rate of 50°C per hour and then maintained at that temperature for 5 hours, to thus remove organic substances.

The gel from which the organic substances were removed was sintered in a sintering furnace under a chlorine gas atmosphere and controlled at a temperature of about 1000 °C for about 5 hours to remove a hydroxy group. Thereafter, a sintering process was carried out in a sintering furnace controlled at a temperature of about 1450 °C and a helium gas atmosphere, for glassification.

COMPARATIVE EXAMPLE

This embodiment was carried out in the same manner as described in Example 2, with the exception of fumed silica being used as silica.

In the Example 2 and the Comparative Example, the content of silica solid in the sol, and the green density thereof after removing organic substances (based on the density of a sintered body), were measured.

As a result, it was observed that the content of the silica solid in the sol was about 46 % and the green density of the gel was about 35 % in the Comparative Example, and that the content of the silica solid in the sol was about 55 % and the green density of the gel was about 42 % in the Example 2.

Also, it was observed whether cracks and shrinking of silica glass overcladding tubes manufactured by the Example 2 and Comparative Example generated.

5 As a result, cracks after drying scarcely occur in the overcladding tube manufactured by the example 2, unlike the overcladding tube manufactured by the comparative example. Also, the shrinking ratio of the overcladding tube manufactured by the example 2 was 24% and the shrinking ratio of the overcladding tube manufactured by the Comparative Example was 28%. Thus, the shrinking ratio of the overcladding tube manufactured by the example 2 is far lower than that
10 of the overcladding tube manufactured by the comparative Example.

Therefore, a high purity silica glass tube, in which cracking after drying scarcely occur and shrinking ratio is remarkably decreased, can be obtained by using the silica glass composition according to the present invention. Also, a large silica glass tube can be manufactured by using the composition.

15 The silica glass obtained by the manufacturing method according to the present invention can be applied to a silica glass for semiconductor devices, an optical lens and so on as well as for an optical fiber preform.

CLAIMS

1
2 1. A silica glass composition comprising:
3 pyrogenetic silica having an average particle diameter of 5×10^{-3} to $1 \times 10^{-1} \mu\text{m}$
4 and a specific surface area of 50 to 400 m^2/g ; and
5 heat-treated silica as an agglomerate of the pyrogenetic silica, having an
6 average diameter of 2 to 15 μm and a specific surface area less than that of the
7 pyrogenetic silica.

8
1 2. The silica glass composition according to claim 1, wherein the mixing
2 ratio by weight of the pyrogenetic silica to the heat-treated silica is 1:10 to 1:1.

1 3. The silica glass composition according to claim 1 or claim 2, for use in
2 manufacturing optical fiber.

1 4. A method for preparing silica glass comprising the steps of:
2 (a) forming a sol by mixing a dispersion medium and a mixture of pyrogenetic
3 silica having an average particle diameter of 5×10^{-3} to $1 \times 10^{-1} \mu\text{m}$ and a specific
4 surface area of 50 to 400 m^2/g and heat-treated silica as an agglomerate of the
5 pyrogenetic silica having an average diameter of 2 to 15 μm , and a specific surface
6 area less than that of the pyrogenetic silica;
7 (b) aging the sol;
8 (c) removing air bubbles from the aging-treated sol and gelling the same to
9 form a gel; and
10 (d) drying the gel and then heat-treating the dried gel.

11
1 5. The method according to claim 4, wherein in step (a), the mixing ratio
2 by weight of the pyrogenetic silica to the heat-treated silica is 1:10 to 1:1.

1 6. The method according to claim 4 or claim 5, wherein in step (a), the
2 heat-treated silica is manufactured by the steps of:
3 (a-1) adding deionized water to the pyrogenetic silica and then mixing the
4 resultant;

5 (b-1) drying the resultant obtained in step (a-1) and selecting particles having
6 a predetermined particle diameter; and

7 (c-1) heat-treating the resultant obtained in step (b-1) at a temperature in the
8 range of 500 to 1200 °C.

1 7. The method according to claim 6, wherein in step (a-1), the mixing ratio
2 by weight of the pyrogenetic silica to the deionized water is 1:10 to 1:5.

1 8. The method according to claim 6 or claim 7, wherein in step (b-1), the
2 average particle diameter of the particles is in the range of 10 to 850 μm .

1 9. The method according to claim 4 or any claim dependent therefrom,
2 wherein the step (b) is achieved at temperature in the range of 15° to 50°C.

1 10. A silica glass generally as herein described.

1 11. Methods generally as herein described.



Application No: GB 9821106.3
Claims searched: 1-11

Examiner: Dr. Guy Standen
Date of search: 2 December 1998

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.P): C1A (APB1, APB5) C1M (MCC)

Int CI (Ed.6): C01B (33/14, 33/141, 33/146) C03B (37/016)

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 0800748 COLUMBIA-SOUTHERN CHEM CORP. see page 2, lines 102-108	1 at least

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined
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A Document indicating technological background and/or state of the art.
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E Patent document published on or after, but with priority date earlier
than, the filing date of this application.